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THEORETICAL ASPECTS OF
ATOMIC COLLISIONS; II

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SRCC REPORT NO. 58 END

UNIVERSITY OF PITTSBURGH
PITTSBURGH, PENNSYLVANIA

6 OCTOBER 1967

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THEORETICAL ASPECTS OF ATOMIC COLLISIONS II

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ABSTRACT

This report contains the text of an invited paper presented to the Plenary Session 5-1-P of the Fifth International Conference on the Physics of Electronic and Atomic Collisions, Leningrad, USSR, July 17-23, 1967. A series of three invited talks (by three different speakers) summarizing the theoretical contributions to the Leningrad Conference were delivered at this Plenary Session. The talk embodied in this report, the second of the aforementioned series, concentrates on the relatively unconventional theoretical papers heard at Leningrad. More precisely, this talk concentrates on recent developments falling under the three headings: (1) classical methods; (2) variational methods and bounds; (3) Faddeev equations. In general, topics falling under these headings lie somewhat further from the present mainstream of atomic collision theory than do most topics in the theory of atomic collisions.

The topics I shall discuss fall roughly under the following headings:

1. Classical methods

2. Variational methods and bounds

3. Faddeev equations

In particular, this talk will describe the activity and recent developments in these topics, especially as exemplified by papers presented at this Conference.

The aforementioned topics have been thrown into the same grab bag because, though meriting discussion, they probably are somewhat further from the present mainstream of atomic collision theory than the topics Drukarev treated or Demkov will treat. You will realize, however, that my alloted time does not permit more than a sampling of topics and papers; certainly I don't want to give the impression that the specific works I shall discuss have any major claim to novelty and/or importance. Actually, for the most part, though not entirely, the material I shall talk about has present relevance only for electron-atom collision theory; in other words, my material probably relates more closely to the preceding talk than to the one which follows.

Now let me discuss the first topic I listed, namely classical methods. In this connection one name which must be mentioned is Gryzinski, even though he is not giving a paper at this Conference. Since about the time of the Quebec Conference two years ago, there has been a remarkable surge of interest in Gryzinski's procedures.[1] Briefly, Gryzinski attempts to calculate cross sections for quite complicated collisions by extremely simple and wholly classical methods, in which Planck's constant is never explicitly mentioned. His techniques primarily are adopted to reactions wherein an electron in a

neutral target atom or molecule makes a transition under bombardment by an incident electron or ion. According to Gryzinski, in such collisions the main requirement is knowledge of the effective cross section $\sigma_{\Delta E}$ -- for energy transfer ΔE -- during a classical two-particle Coulomb collision between the incident charged particle and the target electron. The required $\sigma_{\Delta E}$ usually is readily calculated, and often even is expressible in closed form. Once $\sigma_{\Delta E}$ has been obtained, the desired cross section merely is the integral of $\sigma_{\Delta E}$ over the range of ΔE corresponding to the process in question. Deciding on the proper range of ΔE can be a serious difficulty in actual application of Gryzinski's methods, but sometimes the range of ΔE is obvious, as for instance in ionization without electron exchange, when the permitted range of ΔE runs from the ionization energy to the incident ion energy. In other types of reactions, for instance charge transfer, Gryzinski's rules for the range of ΔE seem more ad hoc and less justifiable.

Now as a matter of fact, a paper at this Conference by Garcia, Welker and myself[2] shows that for charge transfer to protons from noble gases and alkali atoms, Gryzinski's methods are not very reliable, although occasional illustrations of remarkable agreement are found.[3] For proton ionization of these same targets, on the other hand, Gryzinski's procedures are much more reliable,[4] certainly to within a factor of 2 or 3. A similar factor has been reported -- by Bauer and Bartky[5] in 1965 -- for the reliability of Gryzinski's procedures in electron ionization. Moreover, it is shown in another paper at this Conference -- by Garcia and myself[6] -- that for ionization Gryzinski's seemingly wholly non-quantal description can be inferred from the quantum expression for the ionization cross section, via a succession of quite reasonable approximations.

The upshot of all this, and of other recently published work by Vriens[7] among others, is that Gryzinski's methods may be better than they appear at first sight, and that they need further critical study, which I hope they will get because Gryzinski's estimates are being increasingly employed in practical application.[8] As pointed out by many of the invited speakers, for instance Golovin,[9] Branscomb[10] and Donahue,[11] these are fields which desperately need atomic collision cross section estimates and are willing to accept what they can get right now, even though the numbers come from calculations which are less accurate or less defensible than the prouder theorists among us like to admit.

In connection with assessments of Gryzinski's methods, I hardly need to note that -- for any given type of reaction -- the failure of Gryzinski's prescription need not mean the idea of estimating the cross section non-quantally is wholly bad; it is conceivable that Gryzinski's prescriptions simply are too crude to do the classical model justice. Thus Bates and Mapleton[12] recently have proposed an interesting alternative to Gryzinski's classical treatment of charge transfer, based on a 40 year old almost forgotten paper of L. H. Thomas.[13] Similarly, at this Conference, Percival and Richards[14] have used a 40 year old paper by R. H. Fowler[15] to make classical estimates of transition rates induced in atomic hydrogen by very slow incident electrons or protons, in which circumstance Gryzinski's purely binary encounter prescription clearly is invalid. Another approach, also fostered by Percival,[16] is to find the probabilities of various reactions -- in for instance the collisions of protons with hydrogen atoms -- by exact numerical integration of the classical three body problem, starting with a very distant proton incident at specified impact parameter and initial velocity. This problem would be determinate, and there would be no sense in talking about

reaction probabilities, if the position and velocity of the atomic electron were known. According to Percival, however, and to the aforementioned Bates and Mapleton[12] paper, one only can assert that the electron is a member of a microcanonical ensemble at the initial bound state energy.

This program of Percival's amounts to accepting Gryzinski's thesis that the collisions are classical, while refusing to accept his further simplifying assumptions. Since the actual collisions do involve Planck's constant, it is not obvious that Percival's more arduous computations will be any closer to experiment than Gryzinski's easily evaluated estimates. Nevertheless, Percival seems to have the computer time and the Perciverence to see his program through. Specifically, a paper on cross sections for positronium formation in e^+ - H collisions, calculated in the fashion I've described, was presented by Percival and Valentine[17] at this Conference. Furthermore, theorists present at the end of session 1-(3) on Monday were privileged to see a film showing the temporal evolution of various types of reactions in electron and positron collisions with atomic hydrogen, performed by the computer under Percival's direction. Myself, I thought the plot was terrific, but I wasn't impressed by the acting.

I now turn to the topic of variational methods and bounds. An invited paper on this subject -- which I would do best to merely parrot because I am not going to improve on it -- was delivered by Spruch[18] at this Conference. Spruch, who is one of the principal originators of theorems on cross section bounds, pointed out that there are two types of such theorems. Some bounds -- like the well-known fact that the elastic cross section for s-wave scattering can't exceed $4\pi/k^2$, k the wave number -- are essentially geometric and are not connected with variational principles. In other cases, however, the bound is a function of a parameter, whose best value -- yielding the best

bound -- is found by differentiating the function; in other words, this second type of bound is connected with a variational principle. Spruch also pointed out that not all variational principles yield bounds. To have an upper bound on the cross section σ, for example, one must know that the variational estimate of σ is surely larger than its true value. Usually, variational estimates do not have any such property. Sometimes, as occurred with the Kohn variational principle for the elastic scattering phase shift at zero energy, they have the desired property,[19] but it takes us a long time to realize it.

Forgetting about bounds for the moment, there arises an obvious question. Granted we can usefully employ a variational principle for some quantity, the cross section σ say, how do we find the particular functional form

$$\sigma = f(\phi)$$

making σ stationary, where φ is the wave function determining σ? For a long time it seemed that the only way to find a variational principle was to try one possible f after another until, by good fortune, an f making σ stationary was hit upon. For instance, I am pretty sure that the Kohn[20] and Schwinger[21] variational principles for scattering amplitudes and phase shifts were found in this fashion, some 20 years ago. More recently, however, routine techniques for constructing variational principles have been developed.[22] To give just one illustration of this assertion, there is a routine procedure for constructing a variational principle for any matrix element

$$W_{ij} = \langle \phi_i | W | \phi_j \rangle$$

of an arbitrary operator W, where one knows merely that ϕ_i and ϕ_j are

respectively the ith and jth bound state eigenfunctions of a given Hamiltonian H too complicated to be exactly solvable. As a matter of fact, what in effect are variational principles of this sort were employed by Chen and Rotenberg[23] in their paper at this Conference. In this fashion, after using the Feshbach[24] projection operator formalism mentioned by Drukarev[25] -- which converts the problem of determining electron scattering resonances into a bound state eigenvalue problem -- Chen and Rotenberg were able to obtain good estimates of resonant level widths in the scattering of electrons by hydrogen atoms.

Formally, the existence of resonances is associated with complex poles of the scattering matrix,[26] regarded as an analytic function of energy. Because the Hamiltonian describing any collision is known to be Hermitian, all actual bound state eigenfucntions of this Hamiltonian must correspond to purely real eigenvalues. Thus the eigenfunction ϕ_r satisfying

$$(H - E_r)\phi_r = 0$$

for any resonant energy E_r cannot be quadratically integrable; in fact, ϕ_r will diverge exponentially at infinity. Because of this complication, construction of a variational principle for E_r has proved difficult, despite our aforementioned recently gained general understanding of the techniques for constructing variational principles.

The Feshbach[24] projection operator technique gets around the above divergence difficulty by in effect constructing[27] a new Hamiltonian having a true purely real bound state eigenvalue at an energy E_r close to, but not necessarily identical with, the real part of E_r. In other words, the resonance energies calculated by the projection operator technique involves so-called level shifts. A possibility for avoiding the divergences without introducing

energy level shifts is to cut off the interaction potential outside some radius R, after which the region from R to infinity effectively can be eliminated from the problem. In this way, Herzenberg and Mandl,[28] a few years ago, constructed a variational principle for the resonant energy E_r which -- because it involved integrals from 0 to R only -- contained no divergent expressions and required no projection operators, even though the variational estimate was a functional of a ϕ_r growing exponentially at infinity. Herzenberg and/or Mandl have made numerous applications of their variational principle, including the applications to low energy electron scattering by molecular nitrogen reported in the paper by Bardsly, Mandl and Wood[29] at this Conference.

However, the need for introducing a cutoff radius into the Herzenberg-Mandl variational principle obviously raises awkward questions about the precise meaning of results obtained with this principle; at the very least one must be sure the answers don't depend on the choice of cutoff radius, as Herzenberg and Mandl of course realized. But investigating the dependence on R means extra work, and in any event the whole idea of introducing a parameter on which results are supposed not to depend is esthetically unpleasing to we beauty-loving theorists. For this reason, the joint contributions of Rudakov[30] and Kutchinsky[31] at this Conference are worth mentioning, because they apparently construct a variational principle for complex E_r without employing either cutoff radii or projection operators. Because I have seen very few details, all I can say about this variational principle is that it apparently involves a feature very unusual in variational principles, namely analytic continuation[32] in the complex energy plane.

Now what about bounds? Unfortunately, we have no general techniques

for obtaining variational bounds in the phase shifts, level widths, oscillator strengths, etc., of interest in atomic collision theory. By and large, the problem of finding bounds still is at the stage of trying one manipulative trick after another, usually to no avail. This is unfortunate because in the present state of atomic collision theory variational bounds offer almost the only means of estimating approximation errors, or of deciding without hand waving whether suggested improvements of the theory really have any merit.

Still, as Spruch discussed in his invited paper,[18] bounds on some quantities of interest have been established. For example, the dispersion relation connecting the real and imaginary parts of the scattering amplitude yields a bound, in this case non-variational, on the zero energy elastic scattering amplitude. Another class of bounds on scattering phase shifts, for finite energies this time,[33,34] is obtained from the close coupling calculations Drukarev[25] has described. I also want to mention two quite novel bounds which are derived in papers at this Conference. Kleinman, Hahn and Spruch[35] have found upper and lower bounds in the coefficient of r^{-6} in the expansion, at large r, of the interaction potential between an electron and a spherically symmetric atom. Aspinall and Percival,[36] for problems which may be treated in an impact parameter formulation, have obtained a formula yielding an upper bound on the total inelastic cross section, and have applied their formula to inelastic collisions of H(1s) with H(1s).

My last topic is the Faddeev equations, which were discussed by Faddeev himself in an invited paper. For about 20 years now, the starting point for many scattering calculations has been the Lippmann-Schwinger[37] integral equation. The presumed advantage of the Lippmann-Schwinger integral

equation -- over the Schrodinger differential equation it replaces -- is that solutions to the integral equation automatically satisfy the boundary conditions. But about ten years ago it became apparent that this presumption was incorrect for collisions involving more than two particles, i.e., for collisions more complicated than potential scattering. In fact, for three or more interacting particles, solutions to the Lippmann-Schwinger equation simply are not unique.[38] Faddeev's contribution,[39] in about 1960, was to reformulate the integral equation for three -- and only three -- interacting particles so as to eliminate this difficulty. Solutions to the Faddeev equations are unique, and they do automatically satisfy the required boundary condition.

Actually Faddeev's reformulation produces three coupled integral equations in three unknown quantities, which is why we speak of the Faddeev equations -- plural -- but this is just a detail. More significant is the fact that the kernels of these three-particle integral equations now involve explicitly the exact two-particle scattering operators. This can be seen to make very good sense physically; indeed, wholly ignoring the uniqueness question, the Faddeev equations do appear to express the actual physical situation much better than did the Lippmann-Schwinger equation.

There are good mathematical and physical reasons, therefore, to hope that the Faddeev equations can become the basis for improved calculations of three-particle scattering cross sections. Unfortunately, the very features that make the Faddeev equations so appealing physically simultaneously make very difficult any actual computations with them; a triad of integral equations coupled through hypergeometric functions -- the Coulomb two-body scattering operators -- are not readily made tractable. Nevertheless, this Conference has seen very considerable progress in the application

of Faddeev's equations to atomic collision theory. In particular, McCarroll and Salin[40] have taken advantage of the fact that, because the electron mass is so much smaller than the proton mass, the Faddeev equations considerably simplify[41] for proton-hydrogen atom collisions. In this way, McCarroll and Salin have been able to obtain some interesting results on the high energy behavior of the p-H charge transfer cross section.

A very different kind of approximation has been employed by Ball, Chen and Wong[42] in electron-hydrogen atom scattering. They approximate the exact two-body Coulomb scattering operator in the Faddeev equation kernels by a finite series of terms, whose form is such that the Faddeev equations then reduce to a set of coupled one-variable integral equations, which can be handled in a computer without too much trouble. Using a series of only six terms they are able to make surprisingly accurate predictions of the binding energy of H^{−}, as well as of the lowest e-H resonance energy. Another interesting feature of their work is that (as originally suggested by Rotenberg[43]) they expand in a series of so-called Sturmian functions, which are hydrogenic wave functions except that instead of the energy the charge is regarded as the eigenvalue. The advantage[43] of the Sturmian functions is that they form a discrete complete set; when expanding in Sturmian functions there is no need to explicitly introduce an integral over a continuous spectrum. Sturmian functions also were employed by Gallaher and Wilets[44] in their impact parameter calculations of proton-atomic hydrogen scattering. I predict increasing use of these functions in the next few years.

I will conclude with the remark that Faddeev's equations can be generalized to systems of four or more particles.[45] However, the Faddeev equations for four-particle scattering explicitly involves the exact three-particle scattering operators, and similarly for scattering of larger numbers of particles. Thus it is very unlikely that the Faddeev equations will have any practical application in atomic collisions bringing together more than three interacting particles.

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